The Vapor Pressures of Aqueous Solutions of Electrolytes

By EDWARD OTTO HEUSE
B.S. HANOVER COLLEGE, 1900
M.S. UNIVERSITY OF ILLINOIS, 1907

THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS

1914

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The Vapor Pressures of Aqueous Solutions of Electrolytes.[1]

CONTENTS.—1. Purpose and Outline of the Investigation. 2. Outline of the Method. 3. Calculation of the Relative Vapor Pressure Lowering. 4. Description of the Apparatus. 5. Testing the Apparatus. 6. The Vapor Pressures and Osmotic Pressures of Cane Sugar Solutions. 7. The Vapor Pressures of Potassium Chloride Solutions. 8. The Vapor Pressures of Lithium Chloride Solutions. 9. Discussion of Results. 10. Summary.

1. Purpose and Outline of the Investigation.

The primary purpose of this investigation is the study of the condition of dissolved substances in aqueous solution, with especial reference to the question of the extent and nature of the union between solvent and solute in the solution: For such an investigation, there are theoretically available four principal methods of attack. These are the methods of freezing point lowering, boiling point raising, osmotic pressure, and vapor pressure lowering.

The first two—the freezing point and the boiling point methods—have the disadvantage that it is necessary to change the temperature and the concentration of the solution simultaneously, while the method of osmotic pressure has only a limited applicability, because of the difficulty of preparing suitable semi-permeable membranes. The boiling point method also has the disadvantage that the boiling point changes quite considerably with changes in atmospheric pressure.

With the method of vapor pressure lowering, the concentration of the solution may be changed at will without changing the temperature, and it is also possible to make determinations for one concentration over a large range of temperature. Several methods for the measurement of vapor pressure of solutions have been proposed by various investigators, and the study of one of these—the air-saturation, or dynamic method—was undertaken in this laboratory several years ago,[2] and an apparatus developed which proved sufficiently accurate to warrant further prosecution of the investigation by this method. The present undertaking is, therefore, really a continuation of the previous investigation with some modifications and improvements in the method and apparatus, that were suggested by the previous work. Using this improved apparatus, I have undertaken to measure the vapor pressure lowering produced by uni-univalent electrolytes in aqueous solution of moderate concentrations.

[1] Under the title "The Measurement of Vapor Pressure Lowering by the Air Saturation Method," Parts 1–6 of this thesis were published in *J. Am. Chem. Soc.*, **37**, 309–321 (1915).

[2] H. B. Gordon, Univ. of Ill. Theses, 1912.

For the purpose of securing a reference curve, some determinations were also made of the vapor pressure lowering produced by cane sugar.

2. Outline of the Method.

The dynamic or air-saturation method when employed for the purpose of measuring the difference between the vapor pressure (p_0) of a solvent and that (p) of a solution has usually been carried out by determining each of these quantities separately and then subtracting one from the other. This procedure gives a very low degree of accuracy on the vapor pressure lowering, the chief sources of error being (1) in the measurement of the quantity of air aspirated and (2) in maintaining the average temperature of two successive experiments sufficiently constant. The obvious modification which is necessary in order to eliminate these two sources of error is to pass the same air (whose quantity, therefore, need not be known) over the solution and the solvent in succession, each liquid being contained in a suitable "saturator" and both saturators being placed beside each other in a well-stirred thermostat. Then one may either determine the losses in weight of the two saturators by weighing them before and after the experiment, as in the method of Ostwald-Walker or one may absorb the moisture in absorbers of such form and size that they can be accurately weighed. The former method has been successfully carried out by Berkeley, Hartley and Burton[1] with aqueous solutions at 0°. The latter method seemed preferable to us, however, because it involved no change in the concentration of the solution during the run and the volume of air and its rate of flow could be made as large as desired, since there was no necessity of employing a small and compact saturator as is the case when the saturator has to be weighed.

Our apparatus, therefore, has been constructed so as to embody the advantages of the differential procedure first used by Ostwald and Walker with those of the absorption method which has been employed by most investigators in this field. The type of absorber which we have employed coupled with the comparatively high rate of aspiration used necessitates the use of small differential manometers for the purpose of measuring the fall in pressure through the apparatus. With a different type of absorber cooled with liquid air, these manometers could probably be dispensed with.

3. Calculation of the Relative Vapor Pressure Lowering.

The following method of computing the results of an experiment conducted as outlined above is applicable to moderate temperatures: At high temperatures, where the deviation of saturated water vapor from Boyle's law is large, corresponding modifications must be made in the method of calculation, but these will not be entered into here.

[1] Berkeley, Hartley and Burton, *Phil. Trans.*, (*A*) **209**, 177 (1909).

The mass, m, of water necessary to saturate a volume, v, of air in order to bring it into equilibrium with a liquid whose aqueous vapor pressure is p is expressed by the equation

$$m = Kpv \tag{1}$$

where K is a proportionality constant. In the method just outlined the same air is passed through both saturators and hence the volume emerging from a saturator will vary inversely as the partial pressure of the air in that saturator. Obviously, this is in each case the atmospheric pressure diminished by the vapor pressure of the liquid with which the air is in equilibrium and by the difference between the total pressure within the saturator and the atmospheric pressure. It therefore follows that

$$\frac{v_1}{v_2} = \frac{B - p_2 - \Delta P_2}{B - p_1 - \Delta P_1} \tag{2}$$

where the subscripts indicate whether the quantity is measured at the outlet of the first or the second saturator of the train. B is the barometric pressure and ΔP the difference between this pressure and that within the saturator as measured by a differential manometer.

From (1) it follows that the ratio of the masses of water absorbed by the two absorbers will be

$$\frac{m_1}{m_2} = \frac{p_1 v_1}{p_2 v_2}. \tag{3}$$

If the second saturator contains pure water ($p_2 = p_0$) and the first saturator an aqueous solution ($p_1 = p$), we have from (2) and (3)

$$p = \frac{m p_0 (B - \Delta P_1)}{m_0 (B - p_0 - \Delta P_2) + m p_0}. \tag{4}$$

Dividing both sides of Equation 4 by p_0, subtracting each side from unity, expressing the result in the fractional form and collecting terms, we have

$$r = \frac{p_0 - p}{p_0} = \frac{(m - m_0)p_0 + m_0(B - \Delta P_2) - m(B - \Delta P_1)}{(m - m_0)p_0 + m_0(B - \Delta P_2)}. \tag{5}$$

Putting $m_0 - m = D_m$ and $\Delta P_2 - \Delta P_1 = D_p$ gives

$$r = \frac{p_0 - p}{p_0} = \frac{D_m(B - \Delta P_1 - p_0) - m_0 D_p}{m_0(B - \Delta P_2) - D_m p_0}. \tag{6}$$

This is the expression for $\frac{p_0 - p}{p_0}$ in terms of the quantities which are directly measured in the experiment. In order to make clear the relative importance of the different terms in this expression and their influences upon the accuracy of the result, we will substitute typical values for them as obtained in an actual experiment in which the solution employed was a molal solution of cane sugar. This gives

$$r = \frac{p_0 - p}{p_0} = \frac{0.2401(749.01 - 0.24 - 23.71) - 11.7458 \times 0.050}{11.7458(749.01 - 0.29) - 0.2401 \times 23.71} =$$

$$\frac{174.1 - 0.59}{8794.2 - 5.6} = \frac{173.5}{878.9} = 0.0197. \quad (7)$$

Suppose, for example, that we desire an accuracy of 1% in value of r. Of the terms appearing in the denominator the last one, $D_m p_0$, is practically negligible in comparison with the first and in the first term the quantity ΔP_2 is practically negligible in comparison with B. At most an accuracy of a few tenths of a mm. in measuring ΔP_2 would be ample, and an accuracy ten times as great as this is easily attained. The degree of accuracy with which the denominator of Equation 6 is known depends, therefore, practically upon the accuracy with which m_0 and B can be measured, and it is clear that both of these quantities can be easily measured with 10 or 100 times the necessary accuracy. As far as the terms in the denominator are concerned we may, therefore, conclude that the errors involved in their measurement will not have any appreciable influence upon the accuracy of the result.

Turning to the numerator we note that the second term, $m_0 D_p$, is very small in comparison with the first, and that at most an accuracy of 0.05 mm. in the measurement of D_p would be ample. This degree of accuracy, and more, can be easily attained. In the first term of the numerator ΔP_1 is practically negligible while p_0, the vapor pressure of the pure solvent at the temperature of the experiment, needs to be known with an accuracy of 7 mm. (*i. e.*, 30%) if it is not to influence the accuracy of the result by more than 1%. In the case of water it is of course known with an accuracy 100 times greater than this and in any case its determination with the necessary degree of accuracy offers no difficulties. We may conclude, therefore, that the percentage accuracy of the result is almost entirely determined by the percentage accuracy attainable in the quantity D_m, that is, the difference in the increases in mass of the two absorbers, and this difference is itself directly determined by placing the absorbers on the opposite pans of a sensitive balance and adding the necessary weights to produce equality. This difference can be determined to 0.1 or 0.2 mg. and in the example taken this would amount to less than 0.1%. Practically, however, the accuracy of the final result is not determined by the accuracy in *measuring* the actual difference, D_m, obtained but rather in insuring such perfect experimental conditions that the observed D_m shall correspond to the actual pressure difference within the required limits. As will be seen later the degree of concordance in duplicate experiments is more nearly 0.5% in the case of a molal solution.

From this discussion of the theory of the differential method the following facts are brought out, which distinguish it from most of the previous

attempts to determine the vapor pressure lowering of aqueous solutions by means of the dynamic or air-saturation method:

(1) It is not necessary to measure or to know even approximately how much air is passed through the system during the experiment, and its amount may, therefore, be made as large as desired.

(2) In order to measure the relative lowering of the vapor pressure the individual vapor pressures themselves are not required, except a very rough value of p_0, the vapor pressure of the pure solvent, an accuracy of a few mm. in the value of p_0 being amply sufficient.

(3) Temperature variations[1] as great as 1° during the course of an experiment would not appreciably influence the result for solutions of moderate concentrations provided the thermostat is kept thoroughly stirred.

4. Description of the Apparatus.

General Arrangement.—In the apparatus now in use *three* saturators are employed in each experiment, the first and third containing pure water and the second the solution under investigation. The general plan of the apparatus is shown diagrammatically in Fig. 1.

Air, drawn by the constant level aspirator B, passes first through the soda lime tube T, and then into the presaturator PS_1, where it is *saturated* with water vapor at about 50°. The air then passes down into the flask F which is immersed in the thermostat and here it deposits most of its excess of moisture and enters the first saturator S_1 of the train slightly supersaturated. On emerging from this saturator it is in equilibrium with water at 25°. It then passes out of the thermostat through the tube C_1, which is surrounded by a heating coil and is heated to a temperature of about 30° before it emerges from the thermostat. The warm air then passes at once through the absorber A_1 where all of the moisture is removed. The perfectly dry air then goes through a second presaturator, PS_2, containing water at 25° where it takes up the bulk of the moisture necessary to bring it into equilibrium with the solution in saturator S_2. After passing through this saturator and its absorber, A_2, the perfectly dry air then passes directly into the third saturator, S_3, which contains pure water. In the first and third saturators equilibrium is always approached from *opposite directions* and a valuable check upon experimental conditions is thus obtained.

[1] The temperature coefficient of $r = \frac{p_0 - p}{p_0}$ is $\frac{100\, dr/dt}{r} = 100\,(1 + 1/r)\,\frac{L_D}{RT^2}$ % per degree where L_D is the differential heat of dilution (heat absorbed) per mole of solvent. At 25° this becomes $\frac{100\, dr/dt}{r} = 5.66.10^{-4}\,(1 + 1/r)\,L_D$. Thus, for a molal cane sugar solution L_D is about 2 cal. and $r = 0.02$. Hence the temperature coefficient of r for this solution is only 0.06% per degree.

The small differential manometers, M_1, M_2, M_3, connected (through stopcocks) as shown, serve to measure from time to time the pressure differences ΔP_1, ΔP_2 and ΔP_3, respectively. All connections under the

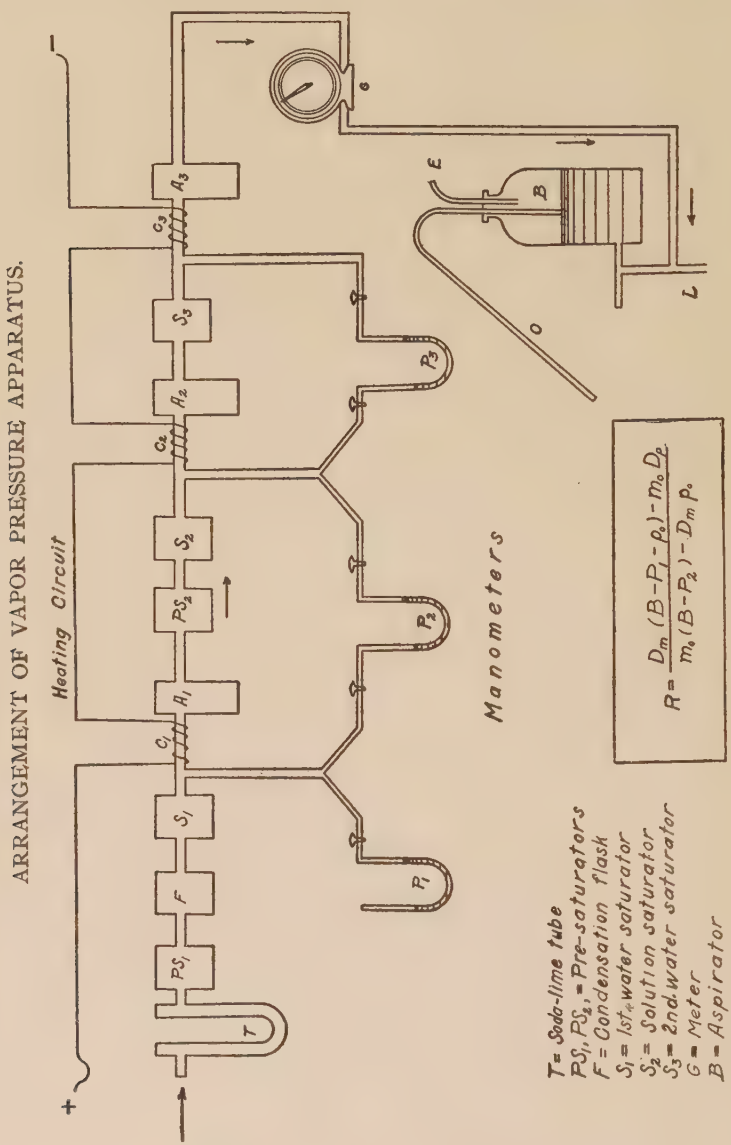

Fig. 1.

water of the thermostat are sealed glass joints, the whole apparatus being supported on a frame as shown in Fig. 2. The details of construction of the different parts follow.

The Saturators.—These are of the type devised by Berkeley and Hartley,[1] modified by the addition of the small bulbs at the ends as shown in Fig. 3 and Fig. 2. The horizontal tubes are filled about half full of

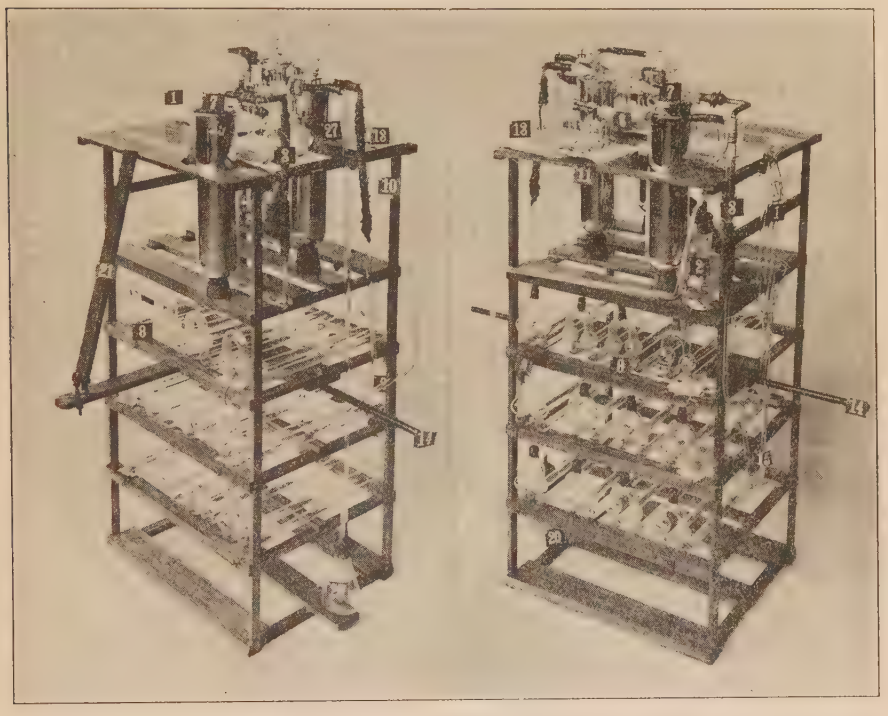

Fig. 2.

(Letters in parentheses refer to Fig. 1.) (1) Tubes leading to manometers. (2) Presaturator (PS_2) for solution. (3) Tube and heating coil (C_2). (6) P_2O_5 safety tube. (8) Saturator (S_3). (9) Point where the air enters the system. (13) Absorber (A_1). (14) Axle on which frame rocks. (20) Condensation flask (F).

liquid and then, as the platform on which the saturators are placed rocks slowly back and forth, the liquid flows from one end of the horizontal tubes to the other. The air which enters at the center of each horizontal tube passes around through

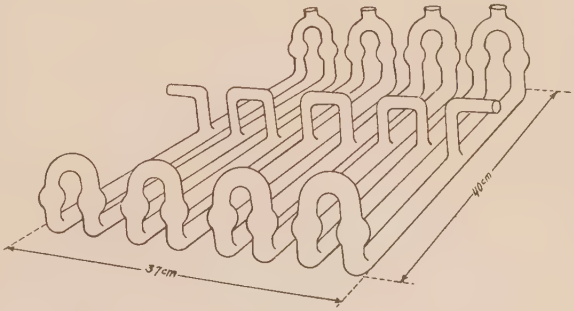

Fig. 3.

[1] Berkeley and Hartley, *Proc. Roy. Soc.*, (*A*) **77**, 156 (1906).

first one vertical connecting tube and then the other as the saturator tips back and forth. The air never bubbles through the liquid at any point. The small bulbs in the vertical connecting tubes are for the purpose of breaking liquid films which sometimes form in the case of certain solutions. The saturator for the solution contains quartz beads which roll back and forth and aid in keeping the solution stirred.

The Absorbers.—The type of absorber used for removing and weighing the water vapor in the experiments recorded below is shown diagrammatically in Fig. 4. Most of the water is condensed in the flask *F*, which is cooled by an ice bath in a silvered Dewar tube. The air then passes over concentrated sulfuric acid contained in the four tubes *A*.

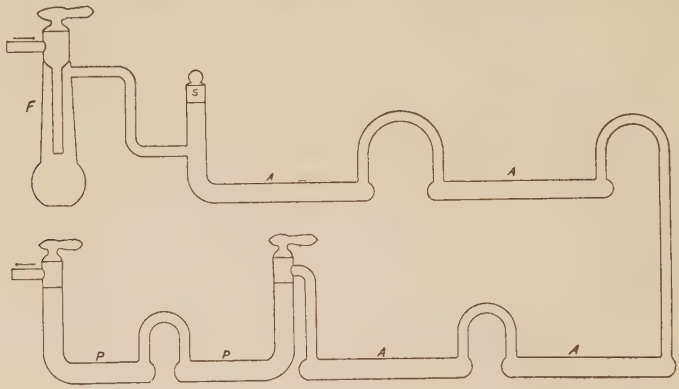

Fig. 4.

These tubes have a series of depressions or pockets (not shown in the figure) along the bottom for increasing the amount of sulfuric acid which they will contain. The two tubes *P* are about two-thirds filled with glass beads and phosphorus pentoxide and a removable pentoxide safety tube (not shown) completes the absorber and serves to prevent the diffusion of any moisture backward against the air current. The absorber is compactly built so that it will fit the pan of a sensitive balance. It is shown in position on the upper shelf of the support, at 13 in Fig. 2. About 25 g. of water can be condensed and absorbed in one absorber. The different absorbers are as nearly identical as possible in construction and when charged ready for use weigh about 300 g. each.

The Differential Manometers.—The small differential manometers, M_1, M_2, M_3, shown in Fig. 1 are water manometers inclined at such an angle that 1 mm. of mercury is equivalent to 200 mm. of water. The angle of inclination was determined accurately by means of a cathetometer. The stopcocks which separate these manometers from the train are opened at intervals during the run and the readings of the manometers recorded.

When the experiment is proceeding properly these readings are practically constant throughout the run.

The Thermostat.—The apparatus and support as shown in Fig. 2 are immersed in a large water bath at such a depth that the three lower platforms and their saturators are completely covered. The whole support is then rocked back and forth on the axle (14, in Fig. 2) at the rate of four complete oscillations per minute. In addition to the stirring produced by this motion two powerful turbine stirrers and one propeller blade stirrer insure a uniform temperature throughout all parts of the thermostat. Three heaters symmetrically distributed and controlled by a hydrogen regulator served to keep the temperature constant.

With this arrangement the apparatus can be kept in continuous operation and as many runs as desired made with a given solution, the air current being interrupted only long enough to replace one set of absorbers by another. When a new solution is to be employed the apparatus is lifted out of the thermostat, the old solution removed with a pipette and the new one introduced. It is not necessary to take the apparatus apart for this operation. Previous to the first insertion of a weighed pair of absorbers in the train the air current is allowed to pass through the system for half an hour to insure equilibrium and proper working conditions. The barometer is read from time to time during the run. In one or two cases the occurrence of thunder storms during the run necessitated the use of a barograph record in finding the weighted time average of the barometric pressure during the run.

5. Testing the Apparatus.

One of the most satisfactory methods of testing the apparatus is to make a run with pure water in all three saturators and then compute the value of $r = \frac{p_0 - p}{p_0}$ by means of Equation 6. The result should, of course, be zero. In seven successive experiments of this kind in which only two saturators were employed Gordon found an average value[1] of 0.026 for 100 r. With the apparatus now in use this has been considerably reduced indicating a more perfect attainment of equilibrium between the liquid and gaseous phases during the passage of the air current. Some typical data of this kind are shown in Table I. When one recalls that the value of 100 r for a molal aqueous solution of a nonelectrolyte is about 2 it is evident that the residual errors indicated by the figures in the last column of Table I would tend to show that the error in measuring the vapor pressure lowering of a molal solution should not exceed one-fourth of 1% on the average.

[1] Gordon, *Loc. cit.*, p. 22, Table III.

TABLE I.—RESULTS WITH WATER IN ALL THREE SATURATORS.

Duration of run.	Saturators used in calculation.	m_0.	Dm.	Volume of air aspirated. Liters.	ΔP_1.[1]	ΔP_2.[1]	ΔP_3.[1]	$100\,r$.[2]
45 hrs.....	1 and 2	18.2417	0.0033					—0.0027
				789.0	0.18	0.33	0.50	
	2 and 3	18.2435	0.0051					0.0041
24 hrs.....	1 and 2	14.9149	0.0031					0.0051
				645.0	0.10	0.21	0.33	
	2 and 3	14.9147	0.0029					0.0025
							Mean value,	0.0036

6. The Vapor Pressures and Osmotic Pressures of Cane Sugar Solutions.

The Experimental Data.—In order that a check upon the reliability of the results obtained with our apparatus might be secured, some measurements were carried out with solutions of cane sugar for the purpose of securing a comparison with the accurate osmotic pressure data obtained by Morse. The sugar employed had been carefully purified and the measurements were made on a weight-molal solution to which 0.1 of 1% of $HgCl_2$ was added. The results obtained are shown in Table II. The average percentage deviation of the individual results from the mean is 0.4% showing that reasonably *concordant* results can be obtained at this concentration. Their *accuracy* can be tested by calculating the corresponding values of the osmotic pressure and comparing with Morse's directly measured values for the same solution.

TABLE II.—VAPOR PRESSURE MEASUREMENTS OF WEIGHT-MOLAL SOLUTIONS OF CANE SUGAR.

Duration. of run.	Saturators used in calculation.	m_0.	Dm.	Volume of air aspirated. Liters.	ΔP_1.	ΔP_2.	ΔP_3.	$100\,r$.	Deviations.
24 hrs.....	1 and 2	11.7458	0.2401					1.974	+0.004
				509	0.24	0.29	0.31		
	2 and 3	11.7432	0.2375					1.957	—0.013
24 hrs.....	1 and 2	11.6451	0.2376					1.965	—0.005
				504	0.39	0.48	0.57		
	2 and 3	11.6464	0.2389					1.975	+0.005
23 hrs.....	1 and 2	4.8408	0.0996	209	0.09	0.13		1.987[1]	+0.017[3]
							Mean,	1.970	+0.008
									=0.4%

POLARISCOPE READINGS FOR THE ABOVE SOLUTIONS.

For the solution used in the	Before the run.	After the run.
1st run.....	356.25°	356.00°
2nd run.....	355.61°	355.58°

[1] The pressures here given are mean values (weighted-time-averages) and are expressed in millimeters of mercury.

[2] $r = (p_0 - p)/p_0$.

[3] Because of the small value of m_0 in this run, this value was given only half-weight in the calculation of the mean.

Osmotic Pressure and Vapor Pressure Lowering.—The osmotic pressure of a solution as directly measured in such experiments as those of Morse is defined by the equation

$$\pi' = P - 1 \tag{8}$$

where P is the pressure (in atmospheres) upon the solution when osmotic equilibrium is attained. The osmotic pressure thus defined is connected with the partial vapor pressure of the solvent by the purely thermodynamic relation[1]

$$\left(\frac{\partial p}{\partial \pi'}\right)_T = -\frac{\overline{V}}{v} \tag{9}$$

where v is the specific volume of the saturated vapor at the temperature T, and $\overline{V}$, the "specific solution volume" of the solvent, is the increase in volume which occurs when 1 g. of the solvent is added to an infinite amount of the solution, under the pressure P.

For saturated water vapor at 25°, we may without appreciable error assume Boyle's law for the small pressure interval here involved and write

$$v = \frac{k}{p}. \tag{10}$$

The constant k is most accurately obtained from the thermodynamic relation

$$k = \frac{L_v p}{T(\partial p/\partial T)_P} \tag{11}$$

where L_v is the latent heat of vaporization. The best available data for water when substituted in this equation give a value of k which is not appreciably different from $RT/18$ which value we shall, therefore, employ.

$\overline{V}$, the specific solution volume of the solvent, will in general be a function of π'. It may be calculated for any solution which contains s per cent. of solute and has the density D_P, by means of the relation

$$\overline{V} = \frac{1}{D_P} + \frac{s}{D_P^2}\left(\frac{dD_P}{ds}\right). \tag{12}$$

For cane sugar solutions the evaluation of $\overline{V}$ at 25° in terms of π would strictly require a knowledge of the proper compressibility coefficients of the solutions at this temperature. No such data seem to be available, but by employing those of Tait[2] for 12.4° an approximate calculation of $\overline{V}$ as a function of π' may be made. In this way we find the following values:

π.....	0	8.44	16.93	22.16	26.52	atmospheres
$\overline{V}$.....	1.0029	1.0056	1.0034	1.0008	0.999	cc.

[1] This rigorously exact relation can be written down immediately with the aid of the perfect thermodynamic engine described in a previous paper (*J. Am. Chem. Soc.*, 32, 467 (1910)) giving a much shorter and more direct derivation than that given by Porter for the relation between these two quantities.

[2] Landolt-Börnstein tables.

By integration between 0 and 27 atmospheres the average value of $\overline{V}$ between these limits is found to be 1.003.

Equation 9, therefore, becomes

$$1.003\, d\pi' = -\frac{RT}{18}\frac{dp}{p} \qquad (13)$$

and on integration gives

$$\pi' = \frac{RT}{18.054}\left[\left(\frac{p_0 - p}{p_0}\right) + \tfrac{1}{2}\left(\frac{p_0 - p}{p_0}\right)^2 + \ldots\right]. \qquad (14)$$

In Table III the values of π' calculated with this equation from the vapor pressure data of Table II are compared with the directly measured values of Morse. The agreement between the two is well within the experimental errors of the vapor pressure data and justifies the conclusion that the values obtained with our apparatus are correct within their own degree of precision.

TABLE III.—COMPARISON OF OSMOTIC PRESSURES CALCULATED FROM VAPOR PRESSURE MEASUREMENTS WITH OSMOTIC PRESSURES OBSERVED.

100 r.	Osmotic pressure calculated.	Osmotic pressure observed (Morse).
1.974	27.01	27.030
1.957	26.77	..
1.965	26.88	...
1.975	27.02	27.076
1.987	27.19	..
Mean,	27.0	27.05
Average deviation,	0.11	
% deviation,	0.4	

7. The Vapor Pressures of Potassium Chloride Solutions.

Materials Used.—The potassium chloride used in this work was Kahlbaum's best grade twice recrystallized from conductivity water. The water used in making up the solutions was a good grade of conductivity water prepared by distilling ordinary distilled water from an alkaline solution of potassium permanganate.

The Experimental Data.—These are given in Table IV.

TABLE IV.—VAPOR PRESSURE MEASUREMENTS OF SOLUTIONS OF POTASSIUM CHLORIDE.

Duration of run. Hrs.	Conc.[1] by wt.	Sats. used in calc.	m_0.	D_m.	Volume of air aspirated. Liters.	ΔP_1.	ΔP_2.	ΔP_3.	100r.
23	1.0296	1 & 2	10.5637	0.3488	455	0.21	0.50	1.77	3.161
	....	2 & 3	10.5789	0.3640	...	....	....	....	3.168
24	....	1 & 2[2]	7.9402	0.2581	345	0.16	0.27	....	3.135
24	0.5073	1 & 2	12.3251	0.1777	530	0.07	0.18	0.30	1.388
	....	2 & 3	12.3280	0.1806	...	....	....	....	1.378
24	....	1 & 2[2]	6.0067	0.0863	260	0.30	0.48	0.95	1.373
22	....	1 & 2[2]	7.0076	0.1007	305	0.17	0.35	....	1.368

[1] *I. e.*, moles of salt per 1000 grams of water.

[2] In these runs, the data are given for only one pair of saturators, the results for the other pair, in each of these cases, being so far different from those here given, as to indicate an accident of some sort during the run.

8. The Vapor Pressures of Lithium Chloride Solutions.

Materials Used.—The lithium chloride was also twice recrystallized as in the case of the potassium chloride, and conductivity water was used in making up the solution. This salt being hygroscopic, the exact concentration of the solution was determined by gravimetric analysis.

The Experimental Data.—These are given in Table V.

TABLE V.—VAPOR PRESSURE MEASUREMENTS OF SOLUTIONS OF LITHIUM CHLORIDE.

Duration of run. Hrs.	Conc.[1] by wt.	Sats. used in calc.	m_o.	D_m.	Volume of air aspirated. Liters.	ΔP_1.	ΔP_2.	ΔP_3.	$100r$.
22	1.020	1 & 2	3.6883	0.1659	160	0.15	0.24	0.30	4.3514
	....	2 & 3	3.6860	0.1636	...	....	....	....	4.2993
24	0.502	1 & 2	4.4714	0.0847	195	0.105	0.21	0.24	1.822
	....	2 & 3	4.4706	0.0839	...	....	....	....	1.813

9. Discussion of Results.

(A) Raoult's Law.—According to Raoult's law of vapor pressure lowering, the relative lowering of the vapor pressure of a solvent caused by dissolving a solute in it, is equal to the mole fraction of the solute in the resulting solutions[2] expressed mathematically, this might be stated thus:

$$\frac{p_o - p}{p} = \frac{n_1}{n_1 + n} = x_1 \qquad (15)$$

In this formula the letters have the following significance:

p_o—The vapor pressure of the pure solvent.

p—The vapor pressure of the solvent from the solution.

n_1—The number of moles of the solute in the solution.

n—The number of moles of the solvent in the solution.

x_1—The mole fraction of the solute in the resulting solution.

This equation is based on the assumption that the thermodynamic environment of the solution remains constant when the mole fraction of the solvent is changed.

From the above formula it may be seen that the curve for $x_1 - r$, *i. e.*, the curve obtained by plotting values of x_1 as abscissas, and values of r as ordinates, would be a straight line with a slope of 45°, as shown by the heavier line in Fig. 5.

(B) Aqueous Solutions of Sucrose.—The experimental data for the solutions used have already been given in Table II. In the $x_1 - r$ graph (Fig. 5), the point indicated by the small square represents the position of the mean value of the vapor pressure lowering. It evidently shows considerable variation from the theoretical curve. If, however, the assumption be made that the sugar exists in the solution as a hexahydrate

[1] *I. e.*, moles of salt per 1000 grams of water.

[2] Washburn, *J. Am. Chem. Soc.*, **32**, 665 (1910).

the mean vapor pressure lowering gives the position in the small triangle,[1] which is evidently in very good agreement with the theoretical curve, which is a further piece of evidence indicating that sugar is probably hydrated in solution to this extent. The fact that this is the same hydrate that exists in solution at 0° C.[2] would seem to indicate that the hydration is a comparatively stable one within the temperature range 0° to 25°.

(C) Aqueous Solutions of Electrolytes.—In order to calculate the mole fraction, when the solute was an electrolyte, it was first necessary to know its degree of dissociation in the solution under investigation. For calculating this use was made of the expression: $\gamma = \frac{\Lambda}{\Lambda_0} \cdot \frac{\lambda}{\lambda_0}$, the use of which for this purpose has been discussed by Washburn.[3] No data for these quantities at 25° being available, use was made of the data for 18°.[4,5]

The data for potassium chloride are given in Table VI. The value of the equivalent conductance (Λ) for each concentration used is given in Column 5 of this table, while the corresponding values of the relative viscosity (λ/λ_0) are found in Column 6, and the resulting values for the degree of dissociation are in Column 7. For calculating the mole fraction of the solute, the following expression is given by Washburn and MacInnes:[6]

$$x_1 = \frac{n_1(1+\gamma)}{\frac{1000}{18} + n_1(1+\gamma)} \qquad (18)$$

The values of 100 x_1, derived by use of this formula, are given in the

[1] The two mole fractions are calculated by means of the two equations:

$$x = \frac{1000}{18} \div \left(\frac{1000}{18} + N_1\right) \qquad (16)$$

$$x = \left(\frac{1000}{18} \div W N_1\right) \div \left(\frac{1000}{18} - W N_1\right) + N_1 \qquad (17)$$

In both of these x represents the mole fraction of the water in a solution containing N_1, moles of sugar per 1000 grams of water. In Equation 17 W is the number of water molecules which unite with one molecule of sugar, hence the free water is $\left(\frac{1000}{18} - W N_1\right)$. By use of these equations, the mole fraction of the sugar if not hydrated is found to be 1.769×10^{-2}; while its mole fraction if it is present as the hexahydrate, *i. e.*, if W = 6 in Equation 17 is found to be 1.979×10^{-2}. The mean value of r is 1.970×10^{-2} as is shown in Table II.

[2] Introd. to Prin. of Phys. Chem. (Washburn), p. 150, Fig. 22.

[3] *J. Am. Chem. Soc.*, **33**, 1461 (1911).

[4] Grüneisen, *Wiss. Abh. d. Phys.-Tech. Reichsanstalt*, **3**, 210 (1900).

[5] Kohlrausch and Maltby, *Ibid.*, **4**, 239 (1905).

[6] MacInnes, *J. Am. Chem. Soc.*, **33**, 1702 (1911).

last column of Table VI; and the values of x_1 as abscissas with the corresponding values of r as ordinates are plotted in Fig. 5.

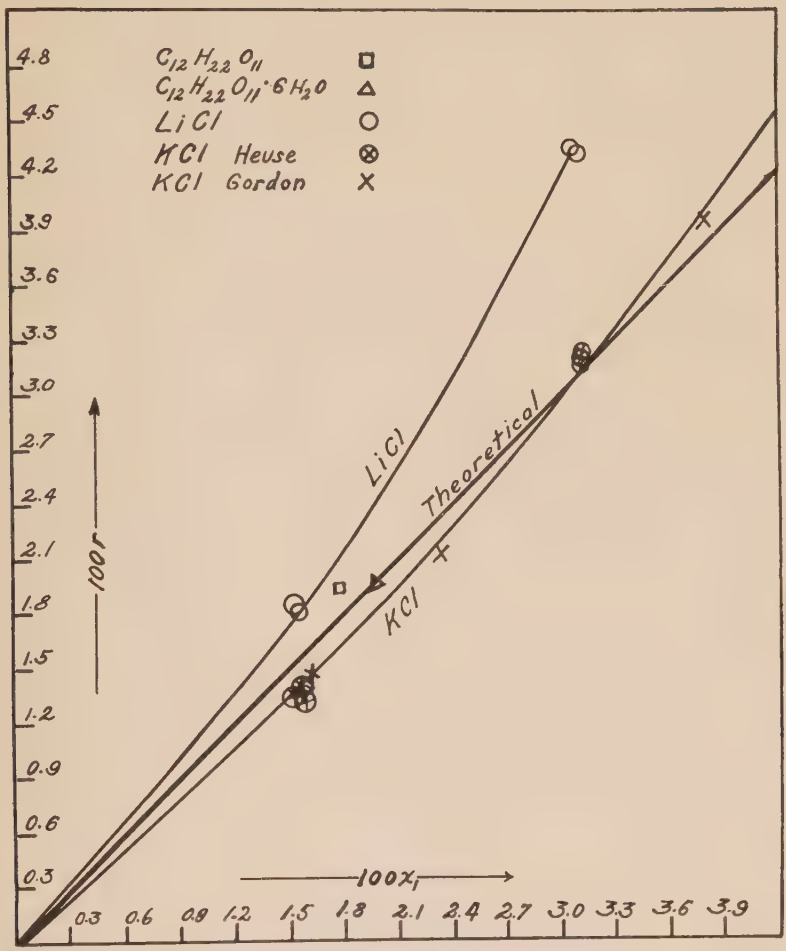

Fig. 5.

From the table, and also from the curve for this salt, it may be seen that for the normal solutions the values of r are within about 1% of the values for x_1, which might be taken as a basis for the conclusion that at this concentration there is no union between solvent and solute. It is known, however, from other work[1] that the ions of potassium chloride are hydrated.

It might also be concluded from the closeness of agreement between the values for x_1 and r that the ions have exactly the same effect on the relative lowering (and so on the other colligative properties, since these are all

[1] Washburn, *Technology Quarterly* and *J. Am. Chem. Soc.*, **31**, 322 (1909).

necessarily connected according to the principles of thermodynamics[1]) as do the undissociated molecules, and that both behave as normal solutes. If this were true it would constitute a real exception to the second law of thermodynamics, since it would require that the mass-action law hold for this solution, which is known not to be the case.

TABLE VI.—RESULTS WITH POTASSIUM CHLORIDE.

Moles of salt per liter of solution.	$100\,r$.	Density of solution.[2]	Moles of salt per 1000 g. of water.	Λ at 18°.[3]	λ/λ_0 at 18°.[4]	$\frac{\Lambda}{\Lambda_0} \cdot \frac{\lambda}{\lambda_0}$ at 18°.	$100\,x_1$.
1.0	3.135	1.0458	1.0296	98.27	0.9820	0.7417	3.130
	3.161	....	....	....	....	....	...
	3.168	....	....	....	....	....	...
0.5	1.388	1.0229	0.5073	102.41	0.9897	0.7790	1.599
	1.378	....	....	....	....	....	...
	1.373	....	....	....	....	....	...
	1.368	....	....	....	....	....	...
0.0	...	....	....	130.1	....	....	...

The values obtained with the half normal solution evidently deviate quite considerably from the theoretical curve, a behavior which is quite different from that found by MacInnes[5] for potassium chloride solutions at 0°. This might possibly be ascribed to error of observation were it not for the fact that the four points obtained agree very closely with one another.

For the purpose of obtaining a check upon these values with potassium chloride solutions, the mole fraction was calculated for some of Gordon's[6] solutions—namely, at concentrations of 0.753 N and 1.290 N. As no conductance data nor viscosity data were available for either of these concentrations, the degree of dissociation for these two solutions was calculated by means of the equation of Kraus and Bray.[7]

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K + D(C\gamma)^m \qquad (19)$$

The left-hand member of this equation is the ordinary mass-action expression, and K the true mass-action constant: while D and m are constants characteristic of the solvent and solute. With water as the solvent, and potassium chloride as the solute, these investigators found D = 2.5, m = 0.67, and K = 0.08.

The values of γ thus obtained were used in the calculation of the mole fraction by the equation given for the normal and half-normal solutions. The resulting values were:

[1] Washburn, *J. Am. Chem. Soc.*, **32**, 496 (1911).
[2] Landolt-Bornstein, Tables, 4th edition.
[3] Grüneisen, *Wiss. Abh. d. Phys.-Tech. Reichsanstalt*, **3**, 210 (1900).
[4] Kohlrausch & Maltby, *Ibid.*, **4**, 239 (1905).
[5] MacInnes, *J. Am. Chem. Soc.*, **33**, 1702 (1911).
[6] Gordon, *Loc. cit.*, p. 22, Table IV.
[7] Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1320 (1913).

Weight concentration.	γ.	$100\,x_1$.	$100\,r$.
0.753 N	0.7595	2.329	2.125
1.290 N	0.725	3.851	3.990

The corresponding points in the $x_1 - r$ graph (Fig. 5) are indicated by the crosses. They are in good agreement with the values for the normal and half-normal solutions as given in Table VI and by the encircled crosses in Fig. 5.

In the case of lithium chloride the degree of dissociation, and the mole fraction of the solute, for the different concentrations used, were calculated in the same manner as in the case of the potassium chloride normal and half-normal solutions.

TABLE VII.—RESULTS WITH LITHIUM CHLORIDE.

Moles of salt per liter of solution.	$100\,r$.	Density of solution.[1]	Moles of salt per 1000 g. of water.	λ/λ_0 at 18°.	Λ at 18°.	$\frac{\Lambda}{\Lambda_0} \cdot \frac{\lambda}{\lambda_0}$ at 18°.	$100\,x_1$.
1.0	4.351	1.0228	1.0201	1.1498	63.36	0.7367	3.090
	4.299	....	....	....	...	.....	...
0.5	1.813	1.0173	0.502	1.075	70.71	0.7687	1.573
	1.822	....	....	....	...	.....	...
0.0	...	....	....	....	98.88	.....	...

The values of the relative vapor pressure lowering given in Column 2, of Table VII, are here again, as in the case of sugar, seen to be considerably larger than the corresponding values for the mole fraction of the solute ($100\,x_1$) which are given in the last column of the table. It can also be seen from the graph (Fig. 5) that the curve for this salt deviates considerably from the theoretical curve.

If this salt were hydrated, the effect on its mole fraction would be the same as was found to occur in the sugar solution, *i. e.*, the value for the mole fraction would be increased, inasmuch as the number of moles of water which act as solvent would be decreased. Thus the denominator in the fraction $n_1/n_1 + n$ would be decreased due to the smaller value for n; and since the value for n_1 would not be affected by this change, the value of the fraction would become larger. It can be seen from Fig. 5 that the deviation which the lithium chloride curve shows from the theoretical curve is a deviation in the direction of a larger value of x_1. Thus it may be concluded that lithium chloride is hydrated when in solution. With the use of the formula

$$x_1 = \frac{n_1\,(1 + \gamma)}{n_1(1 + \gamma) + \frac{1000}{18} - \lambda n_1} \qquad (20)$$

calculation was made to ascertain how many moles of water (λ) would be needed to bring the mole fraction of the lithium chloride in the half-normal solution to the value corresponding to this same value of r on the potassium chloride curve. The value so obtained was about 12, which leads to the conclusion that the degree of hydration of lithium chloride at this concentration is twelve moles more than that of potassium chloride.

[1] Landolt-Bornstein, Tables, 4th edition.

10. Summary.

An apparatus and procedure are described by which it is possible to determine the relative vapor pressure lowering of a normal salt solution with an accuracy of 0.25% and that of a half-normal salt solution with an accuracy of 0.50%. The accuracy of the method is also shown by the results with water in all three saturators, the mean value thus obtained for the relative vapor pressure lowering being 3.6×10^{-5}.

The method is, in brief, the saturating of a current of air by causing it to pass through a saturator containing water and also through one containing a solution, removing the water taken up in each case, and making a comparison between the mass of water taken up by the air in passing through the water saturator and the difference between this mass of water and that taken up in passing through the solution saturator.

The method is such that practically two determinations are obtained from each run, the one by use of a water saturator which the air enters supersaturated, and the other by use of a water saturator which the air enters perfectly dry. These two determinations thus served as a check on each other. The method is also such that the results would not be perceptibly influenced by a slight irregularity in temperature.

The apparatus is so constructed that the total pressure fall throughout the entire system is very small, usually being less than 0.5 mm. of mercury.

By the method here described a check has been secured with the osmotic pressure determinations of Morse, with which the results of this investigation are in practically perfect agreement.

Cane sugar is shown to exist in aqueous solution at 25° C. as the hexahydrate. As this is the same form in which it exists in aqueous solution at 0°, these results show something of the degree of stability of this hydrate over this temperature range.

The results with lithium chloride agree well with the results obtained by MacInnes on the freezing point lowering caused by this salt. This is also true of the normal potassium chloride solution. The 0.5 normal solution shows considerable deviation from the results found by MacInnes, but agrees very well with the results obtained by Gordon by the vapor pressure method, for solutions of potassium chloride of the concentrations 0.753 *N* and 1.290 *N*. It is evident from these results that the vapor pressure lowering cannot be used as a basis for the calculation of the degree of dissociation of the electrolyte.

Lithium chloride in aqueous solution is probably hydrated to quite a large extent, both at normal and half-normal concentrations. Potassium chloride in normal solution seems to agree excellently with the action of a normal solute; this is probably due to a compensation of two opposite influences.

BIOGRAPHICAL.

The writer received his early education in the schools of Madison, Ind. In 1900 he graduated from Hanover College with the degree of Bachelor of Science (cum laude) and in 1906 he received the honorary degree of Master of Arts from the same institution. In 1907 he received the degree of Master of Science in Chemistry from the University of Illinois, his master's thesis having been published, under co-authorship with William M. Dehn, in *J. Am. Chem. Soc.*, **29**, 1137 (1907) under the title, "The Decomposition of Hydrated Ammonium Salts."

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